

THE REDUCTION
OF COTTONSEED OIL

BY
E. W. TURLEY

ARMOUR INSTITUTE OF TECHNOLOGY

1912

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Experimental work on the
reduction of cottonseed oil

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EXPERIMENTAL WORK

on

THE REDUCTION OF COTTONSEED OIL

A THESIS

presented by

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PART I.

There is only one lard compound on the market containing reduced cottonseed oil, namely "Crisco."

EXPERIMENTAL WORK
on
REDUCTION of COTTONSEED OIL.
INTRODUCTION.

The reduction of cottonseed oil on a commercial basis has been in use about one year. This work is the direct result of many years of scientific research in the field of pure chemistry. It is not the work of a single man, but the work of many that has been assembled by a few men who have succeeded in realizing a process of reduction that is practical and profitable to be used commercially.

This problem of reduction involves a thorough and careful study of organic chemistry, chemical dynamics or catalysis, mechanics, electricity, design and practical business knowledge. Therefore this is a true problem in Chemical Engineering.

This problem is in its infancy. The packing houses are the concerns most interested. Their chemists consider this one of the most important

problems.

The only compound of reduced cottonseed oil on the market at present is "Crisco." This is made by Proctor & Gamble Company of Ivorydale, Ohio. They are working under the patents of an Englishman. There is no American to date that has taken out a patent relating to this subject.

"Crisco" has none of the objectionable features which are characteristic of lard and lard compound. Crisco may be heated to 455°F without smoking, while butter smokes at 329°F and lard at 400°F. Lard heated to 455° is discolored and a great quantity of objectionable smoke and odor is given off. Crisco is an economical healthful lard substitute which does not absorb odors and gives to foods a delicate and delightful flavor.

In the process of reduction the iodine number may be made zero. But as some large dealers tell us that the people do not like a substance that is tasteless the iodine number need not be reduced to

zero. This reduced substance may have its iodine number reduced to zero and be used as a basis for other productions which require certain consistency and an odorless and tasteless foundation.

Cottonseed oil is obtained by expression from the seeds of the various kinds of cotton plants grown extensively in America, Egypt and India. The oil is the main product of the seeds. Its specific gravity at $15^{\circ}\text{C}.$ = 0.9229-
^C
 Saponification value = 193; Iodine value = 115;
 Titre at $0^{\circ}\text{C}.$ = 33.6; Refractive index at $20^{\circ}\text{C}.$ = 1.4721. One ton of seed yields 250 pounds of crude oil.

Crude oil-----	300	pounds.
Cake-----	750	"
Lint-----	20	"
Hulls-----	800	"
Loss of waste-----	120	"
Total-----	2000	"

Cottonseed oil consists chiefly of the

glycerides of oleic and linolic acids, the latter as is indicated by the iodine value, being present in greater proportion than in olive oil and amounting to about 17% or 18% of the total fatty acids.

Oil contained in cottonseeds (Lewkowitsch)

Kernels Husks		Oil from		
		Whole Seed	Kernels	Husks
60.0%	40.0%	21.98%	37.41%	0.67%

Since Alkalis are used in refining cottonseed oil, it is practically free from fatty acids. The amount of "stearine" left in the oil determines the proportion of glycerides of solid fatty acids in the oil and the percentage of solid fatty acids vary from 22.3 to 32.6%. The solid fatty acids consist chiefly of palmitic acid; small quantities of stearic acid have also been identified. No linolenic hexambromides have been obtained from cottonseed oil, linolenic acids may be considered as absent. The liquid fatty acids seem to consist of oleic and linolic acid only. The proportion of the mixed fatty acids calculated from the isolated

linolic tetrabromide was found to be 18.45% to 21%. From the liquid fatty acids Farnsteiner obtained linolic tetrabromide corresponding to 23.9% linolic acid. From the percentage composition of 23.45% linolic acid and 76.55% oleic acid would follow the calculated iodine value of the liquid fatty acids = III.5. Since direct experiments lead to the approximate iodine value of the liquid fatty acids of about 150, the amount linolic tetrabromide found would appear to be much below the truth and further experiments are required to explain the apparent discrepancy. The acetyl values vary from 7.6% to 18% according to the freshness of the oil.

The glycerides of solid fatty acids which are present in solution and separate out as "cotton stearine" on chilling the oil consists principally of those of palmitic acid with a small proportion of stearic.

Oils which have been refined by treatment with alkali and separation of "stearin" have a mild taste and are practically devoid of free acids. The solid

esters of cottonseed oil consist mainly of palmitin with a little stearin, the liquid contains ^{oil} ~~often~~ and linolin.

The seed has fiber adhering which is short. These seeds contain considerable foreign matter. Hence they are passed thru revolving sand and boll screen^s. From here they are taken to delinters where the short fibers previously mentioned are removed. The seed goes to hullers or cylinder containing rotary knives in which the husks are removed. By means of a screen hulls and meats are separated. They go to crushers to rupture the oil Cell and reduce to uniform consistency. Then on conveyors to heaters at 75° to 90°C. These are large cast iron steam jacketed kettles with mechanical stirrers. Duration of cooking varies 20 to 30 minutes according to water present in seeds. The object is to expand oil in meats and make them more fluid. Also it coagulates the albumen and drives off the water. Water is not only bad for the oil but works injury to expensive filter cloths. Very dry meats may cook in 12 minutes against 45 minutes for fresh meats. Near

the heaters stands mill for shaping meal for press. After coming from this machine the cakes are wrapped in hair cloth and removed to the press where a pressure of 3000 to 4000 pounds per square inch is applied. Crude oil is sent from press to storage tanks where foreign matter is separated by filter or sedimentation. The crude oil has a ruby red or almost black color; the quality determined by seed and treatment. It is contaminated by moisture, etc, color and mucilagenous material. The value of the oil is determined by the loss on refining, which refining included separation of free fatty acids.

Commercial caustic soda is the common refining agent. Refining consists in agitating by air in the kettles. A weighed quantity of oil with caustic soda is added, in accurate proportion in a kettle similar to a soap kettle in construction. The quantity and strength of Na O H is determined by experiment on small quantity of oil. The calculated amount of caustic is

then added when oil reaches 85°F and oil vigorously agitated. General heat is then applied by open steam and temperature is raised to 125°F general agitation continues until disposition to settle is noted. Agitation is continued until precipitation is complete.

Coloring matter, mucilagenous material, soda soap of oleic acid and excess Na O H solution form sludge. This is raw material for cottonseed oil soapstone. After precipitation and oil is cooled the clear supernatant oil is siphoned off to finishing kettle. Here it is washed free from alkali at temperature not above 105°. First wash water is withdrawn until oil comes. Fresh water is added and agitated by air. After all Na O H is separated by washing and water has settled out, moisture is further removed by applying steam in closed coils. Temperature is brought up to 125° and agitation continued. Difficulty is encountered in removing water and plaster of paris is added and agitated. The oil is then filtered, pressed and is now ready for market.

The press cake is a valuable cattle food but is usually diluted before feeding to stock.

PART II.

General Characteristics of catalytic reactions.

REDUCTION of COTTONSEED OIL . INTRODUCTION .

A great number of chemical reactions commence immediately the different components are brought into contact, while other reactions only appear to take place when external energy of some kind is added from without. For example, chlorine and hydrogen gases combined with appreciable energy when it is applied in the form of heat, light, or electricity. It has always been observed that these gases rapidly unite in the presence of platinum foil, platinum black, or charcoal. On the other hand the rate of transformation is retarded in a remarkable manner when the reacting gases are mixed with a foreign gas like oxygen. The velocity of the reaction is also modified by the form and material of the vessel by which the reaction gases are enclosed. These illustrations are types of a large class of reactions, in which the progress of the chemical transformation is modified by the mere presence of a substance which, after the reaction, has the same chemical composition as at the beginning. It was

formerly thought that such reactions were entirely different in their nature from other chemical changes. Berzelius postulated the existence of a new "innate force" to which he gave the name "catalytic force". "A catalytic agent," said Berzelius, "is a substance which merely by its presence and not through its affinity, has the power, to render active affinities which are latent at ordinary temperatures." As with "affinity," so with "catalysis" the word explains the fact. Also the occult cause theory has been abandoned, it is still necessary to have some word to connote these chemical changes which are influenced by the presence of a "foreign" substance. Mitscherlich proposed the term contact actions. Brodie, cyclic actions; but Berzelius' designation, catalytic action or catalysis, is now in pretty general use. The agent which effects the catalytic action may be called the catalyzer or the catalyst.

The more finely divided the condition of the

catalyzer the larger the surface exposed for a given mass. It is thus made highly probable that there is some close relation between "surface" and "catalytic" action, catalysis being due to the enormous accumulation of energy at the surface of things.

Before taking up this relation more closely, a few words should be added in reference to the idea that in catalysis, intermediate compounds are often formed. Thus, De la Rive thought that when platinum black was charged with oxygen, there was formed a surface layer of oxide. When this was plunged into hydrogen, reduction took place and water was formed.

Bornemann found that platinum charged with oxygen decomposed hydrogen dioxide more rapidly than pure platinum; and Englar and Wohler found that platinum black saturated with oxygen dissolves to some extent in hydrochloric acid and decomposes potassium iodide liberating iodine, the relation corresponding to the compound PtO . Sabatier and Senderens think that in certain organic catalytic

reactions there are intermediate compounds formed. The action of a number of finely divided metals such as iron, cobalt, nickel, copper, platinum, palladium, etc., on a mixture of hydrogen and acetylene giving ethane, probably depends on the formation of hydrides and a number of organic reactions are known in which the existence of intermediate compounds have been established beyond question. Indeed, the intermediate compound conception seems to apply rather to organic than to inorganic catalytic actions.

The one part the catalyst plays during the reaction is shrouded in mystery. The catalyst has the same chemical composition at the end as at the beginning of the reaction. This fact was early recognized. Mrs. Fulhame noticed in 1794 that while water materially affected the oxidation of metal and the reduction of their oxides, the metal still retained its former properties. In 1812 Kirchhof showed that when starch is converted into dextrine and sugar by boiling with dilute acids,

the acid which effects the change remains unaltered.

It must not be concluded that the catalyst is necessarily in the same physical state after the reaction is over. There is much evidence to show that the catalytic agent actually participates in the reaction., A spiral of platinum kept in a jet of hydrogen burning in air becomes corroded and covered with a gray or black powder of metallic platinum. This also occurs when a spiral of platinum is kept 48 hours in the vapour of alcohol. In like manner, De la Rive found that if an electric current be passed alternately in opposite directions in water, both electrodes become covered with a fine dust of platinum, presumably produced by the repeated oxidation and reduction of the platinum. The oxidation of ammonia by freshly prepared chromium sesquioxide is really an alternate series of oxidations to a bright green oxide by the oxygen of the air, and reductions to the ordinary oxide by the hydrogen of the ammonia. The action of cobalt oxide on the hypochlorites appears to consist of a

series of alternate oxidations and reductions. Bielby and Henderson also observed that there is a complete alteration of the physical state of the catalyst when ammonia is decomposed by an agency of the metals. Titherly also found that the decomposition of ammonia by sodamide at dull red heat takes place in a series of stages. The sodamide at first splits up into nitrogen, hydrogen, and sodium; the latter combines with ammonia to re-form sodamide. This in turn is again split up and the cycle of reactions begins anew. The sodamide after the action is of the same chemical composition as before. Many other actions might be cited to illustrate the fact that the catalytic agent actually takes part in the reaction.

When it is known that the catalytic agent is actually involved in the chemical change, Wagner proposed to call the phenomenon pseudo catalysis. Oswald, "catalysis by transvection;" but the above mentioned term, cyclic action, is to be preferred.

A small quantity of the catalytic agent is sufficient to affect the transformation of an indefinite-

ly large quantity of the reacting substance. This fact was recognized by Clement and Desormes in 1806. Ernst has shown that a solution containing 0.0004 grams of colloidal platinum will bring about the combination of ten liters of a mixture of hydrogen and oxygen and that the activity of the colloidal metal is not affected by the process; and 0.00001 grams of potassium permanganate in 10 c.c. of solution accelerates the reduction of mercuric chloride by oxalic acid. Titoff states that the rate of oxidation of an aqueous solution of sodium sulphite is quite perceptibly accelerated in the presence of 0.000000000000001 N - Cu SO_4 or even by merely dipping a strip of clean metallic copper in the water for less than a minute.

In some cases the secondary actions modify the catalytic agent itself. For example Philip's process of manufacture of sulphuric acid by the oxidation of sulphur dioxide with spongy platinum was abandoned because the platinum gradually lost its power. Knietsch has, however, traced

the sickening of the action to arsenical and other impurities in the sulphurous gases employed in the process. When these impurities are removed from the gases, the activity of the platinum remains unimpaired and the process is a commercial success, promising to supplant the cumbrous "lead chamber process." A similar explanation will no doubt account for the gradual diminution of the activity of a platinum plate, when placed in a mixture of hydrogen and oxygen. Certain enzymes also appear to lose their catalytic power after having been in use for some time.

Some catalyzers disappear during the reaction, owing to independent side reactions. This was found to be the case with Ferrous salts in the reaction between potassium permanganate and hydrochloric acid in the Fridel Crafts reaction. In the catalysis of methyl cetate by acetic acid, the catalytic agent is a product of the reaction and the amount of catalyzer in the system is continually increasing as the action goes on.

A catalytic agent is incapable of starting a reaction. It can only modify the velocity of the reaction. Titoff has shown that the rate of oxidation of a solution of sodium sulphite is diminished by purification of the water. It is assumed that, however, the reacting substance be purified, a slow reaction would always take place. Ostwald defines a catalytic agent to be "a substance which changes the velocity of a reaction without itself being changed by the process." This implies that a reaction must not only be possible but actually taking place before the catalytic agent can produce any effect. In other words, a catalytic agent is not capable of starting a reaction. It can only modify the action of a catalyzer to the influence of the whip on a horse or oil on the wheels of a rusty machine. When oiled the machine will go faster in spite of the fact that the energy of the driving spring is not changed. The total energy of the driving spring is not altered by the catalyzer. There

is no direct proof that a mixture of hydrogen and oxygen will combine at ordinary temperatures. If such a combination does take place at ordinary temperatures, the process is too slow to be detected by the analytical methods that are at our disposal.

On the other hand, C. F. Schonbein, J. J. Thompson, H. E. Armstrong and P. Duhem believe that the catalyst can actually start the reaction. There seems to be no particular objection to our extending Ostwald's analogy by assuming that the friction before oiling is so great as to prevent the motion of the machine altogether. A catalytic agent cannot affect the final state of equilibrium. The amount of energy transformed during a chemical reaction depends only on the initial and final state of the system and not on the actual course of the reaction. When chemical energy, for example, is transformed into thermal energy, the amount of heat generated is the same whether it takes place all at once or in steps,

other things being equal, the velocity of chemical reactions would no doubt be proportional to the amount of energy transformed during the process, but the velocity in reality depends upon so many external factors known and unknown that no generalization has yet been formulated. Also the velocity of the chemical action may be modified by the catalytic agent, yet the final state of equilibrium remains unaffected if otherwise we could allow the substance to act alternately with and without the catalyzer and so utilize the process to perform work. This would lead to a perpetual motion, which is presumed to be impossible.

As an illustration, Lemoine found that equilibrium set in at 350° C when 18.6% of hydrogen iodide has decomposed. Hantefenille found that 19% decomposed in the presence of platinum black.

The fact that the catalytic agent can have no influence on the numerical value of the equilibrium constant might be employed in doubtful cases

as a test for catalytic actions. If a substance changes the velocity of the reaction and at the same time has no influence on the equilibrium constant, we are dealing with catalysis pure and simple.

Many apparent exceptions to this might occur in the literature of chemistry and these will be found on closer examination to be founded upon imperfect observations.

The velocity of two inverse reactions is effected by the catalyst to the same extent. The condition of equilibrium of the reversible action may be written where

C_{SO_2} , C_{O_2} , and SO_3 , respectively denote a concentration of the molecules

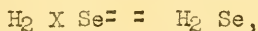
SO_2 , O_2 , and SO_3 , which takes part in the reaction. The rate of decrease of SO_2 and the rate of decomposition of SO_3 are respectively

$$\frac{d C_{SO_2}}{dt} = - k_1 C^2_{SO_2} C_{O_2} ; --$$

$$\frac{d C_{SO_3}}{dt} = - k_2 C^2_{SO_3} .$$

When equilibrium is attained we have equation (1). Since the state of equilibrium is independent of the catalytic agent, the relation between k_1 and k_2 must remain constant, and the velocity of one reaction in the presence of the catalyzer must increase in the same proportion as the other.

W. Micheals found that the velocities of esterification and hydrolysis of an ester at different concentrations were influenced by the catalytic agent in the same way; slight deviations were observed at the higher concentrations. Bodenstein observed the same thing in the reaction



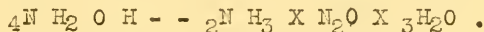
in which the catalytic agent was molten selenium, and R. Knietsch found that the rate of formation of sulphur trioxide from sulphur dioxide and air was slower in the presence of fragments of porcelain than in the presence of platinum and this result is in harmony with the fact that the trioxide decomposes more slowly in the presence of porcelain than in the presence of platinum.

The state of equilibrium is independent of the presence or absence of a catalytic agent. Turbala proved that the equilibrium between aldehyde and paraldehyde was the same whether sulphur dioxide, zinc, sulphate, hydrogen chloride, oxalic acid or phosphoric acid were employed as catalytic agent.

It is easy to see that if side reactions occur, the catalyzer may exercise a specific influence on each, so that the products of the reaction may differ in the presence and in the absence of the catalyzer. For example, an aqueous solution of hydroxylamine decomposes according to the equation -



with the formation and traces of nitrous oxide, thus-



In the presence of oxidizing media or platinum black, the chief product of the action is nitrous oxide. Tanater has shown that a like phenomenon occurs during the catalysis of hydrazine ($\text{N}_2 \text{ H}_4$) .

The phenomenon of catalysis is universal. Ost-

wald says that there is probably no kind of chemical reaction which cannot be influenced catalytically and there is no substance, element, or compound which cannot act as a catalyzer. Ostwald's classification is purely empirical. Henri and Languier and Des Bancel's classification requires more knowledge of the mechanism of each reaction than we possess.

Henri and Languier des Bancel's Classification.

I. Reductions induced by one catalytic agent.

i. Simple contact action. E.g. the action of acids upon an aqueous solution of cane sugar.

ii. Formation of intermediate compounds.
E. g. the action of nitric oxide in the manufacture of sulphuric acid.

II. Relations which take place in the presence of two catalytic agents.

1. The two catalysts produce the same final products.

- i. Simple contact action.
 - a. Catalysts have no action upon one another E. g. the decomposition of hydrogen peroxide by colloidal gold and platinum.
 - b. Catalysts mutually influence each other's action, E.g. the action of a mixture of salts of iron and copper upon hydrogen persulphate and potassium iodide.
- ii. Formation of intermediate compounds.

E. g. the action of acids and of invertin upon cane sugar.
2. The two catalytic agents produce different reactions. E. g. the action of pancreatic juice and of kinase upon a mixture of gelatine and starch.
3. Two consecutive reactions are produced by the two catalytic agents. E.g. the hydrolysis of gentianose by a mixture of emulsin and invertase.

The activity of the catalytic agent depends on its physical condition. The finer its state of division, the greater will be its chemical activity, thus platinum black is far more active than spongy platinum and this in turn is more active than platinum foil. The sharp corners of the catalyst are supposed to break up the molecules into atoms and so render the substance more chemically active. For a given weight of platinum the finer the state of division the greater will be the surface presented to the substance by the catalytic agent.

It has long been known that the course of a chemical reaction is modified by the catalytic action of the walls of the vessel in which the action takes place and Van't Hobb has shown that the disturbing influences depend upon the superficial area and upon the nature of the walls of the vessel in which the reaction takes place. The effect of the walls of the containing vessel upon the course of a reaction may therefore be attributed to various secondary actions.

The molecules at the boundary surface of a liquid medium are not in the same condition as the molecules in the body of the medium. Particles in the body of the medium are attracted in every direction, while those at the surface are only attracted inwards. This inward tension of the surface molecules gives rise to the phenomena of surface tension and of capillarity. J. J. Thomson says that the catalytic effects produced by the walls of the vessel might be attributed in part to the change in physical condition of the molecules of the reacting substance in contact with the surface of the catalytic agent or the walls of the vessel.

Armstrong has amplified De La Rive's suggestion and put forward the hypothesis that two substances will only react in the presence of a surface catalytic agent. Interaction does not take place between pure substances. He assumes that when the complex formed by the association of the interacting substance meet with the neces-

sary third component, a conducting system is established and that as soon as this is formed a change sets in. According to this hypothesis, a circuit of change must comprise three terms or components. One of these must be a conductor of electricity, which is capable of forming with the reacting substance, a system analogous with a closed voltaic circuit. In the case of hydrogen, conducting water and oxygen for example, the withdrawal of moisture renders the combination of hydrogen and oxygen exceedingly difficult.

According to Armstrong's theory, the function of the catalytic agent is to collect in one system, the various elements necessary for a particular chemical change, thus when benzene and methyl chloride are brought into contact there is no chemical action. If, however, aluminum chloride be present, Armstrong assumes that a more or less stable "molecular complex" is formed by the union of the methyl chloride, benzene and aluminum chloride. This too, is the function of impurity in the solution of zinc and sulphuric acid.

Catalytic action of finely divided metals.

A number of interesting experiments have been recently carried out by Bredig, with the cooperation of Von Berneck, Ikeda and Reinder. These authors have studied the catalytic action of finely divided metals, and have pointed out certain analogies between them and organic ferments.

The metals were obtained in a finely divided state in water, by bringing two bars of the metal close together under water and passing an electric current between the bars under the water. The metal was torn off in such a fine state of division that the solution appeared to be perfectly homogeneous when examined under a powerful microscope. Such a solution was shown not to be a true solution, since neither the freezing point nor vapor-tension of the solvent was lowered,. This belongs then to the class of solutions known as colloidal. By this method solutions of platinum, iridium, gold, silver, cadmium, etc were prepared.

Such solutions of the metals, act catalytically,

effecting a number of reactions similar to those brought about by organic ferments. The authors showed that those reactions are truly catalytic, by demonstrating that they are reactions of the first order. The reaction which they studied in detail was the decomposition of hydrogen dioxide by a colloidal solution of platinum. They studied the velocity of the decomposition and found that $\frac{1}{t} \ln \frac{A}{A-x}$ was a constant, and therefore the reaction was of the first order. It is known that colloidal solutions of the metals and organic ferments is found in their behavior in the presence of certain poisons. It is well known that mere traces of certain substances are sufficient to prevent the action of organic ferments; these ferments are poisoned, as we say.

Bredig and his pupils have shown that the merest trace of certain substances is sufficient to diminish greatly the catalytic action of the platinum, and in some cases to destroy it entirely. Thus, a grammolecular weight of hydrogen sulphide in ten million litres of water greatly diminishes the action

of the colloidal solution of the metal. And the same effect is produced by a gram-molecular weight of hydrocyanic acid in twenty million litres of water, and by a number of other substances in very small quantity.

Bredig and Reinders have made an elaborate study of the action of "poisons" on the colloidal solution of platinum, and have found in general that those substances which are most poisonous to the organicenzymes are most "poisonous" to the metal. Some exceptions, were, however, pointed out, but no one can examine the results obtained without being impressed by the large number of agreements.

Bredig is, however, careful to point out in his recent pamphlet on this subject, that the analogy which they have discovered is only an analogy. He does not think that there is any identity between the action of the two classes of substances, which are themselves so different. To quote all his own words - " All these facts point to an unmistakable analogy between the contact actions in the organic world and the actions of ferments in the organic

world. As in the case of my colloidal catalyzers, we are dealing with reactions in which enormously developed surfaces are involved, so it is probably that the same condition obtains in the actions of ferments, enzymes, blood corpuscles, and oxidizing and catalyzing organic substances. Therefore, we see that the organism develops its enormous surface in the tissues and colloidal ferments, not only because it requires osmotic processes, but on account of the very great catalytic activity of such surfaces. If, as Boltzmann says, the war for existence which living matter must wage is a war about free energy, certainly of all the forms of free energy the free energy of "surface" is the most important for the organism.

" In conclusion I need scarcely state that I do not maintain that there is any mysterious identity between the metals and the enzymes; but, without exaggerating the overwhelmingly large number of analogies, we are compelled to regard the colloidal solutions of the metal, in many relations at least, as in-

organic models of the organic enzymes."

It seems that this work may prove to be very important as throwing some light on the nature of enzyme action. The enzymes are very complex organic substances, while the colloidal solutions of the metal are as simple as any substances known to the chemist. If the latter effect reactions analogous to the former, by studying the reactions with the simple elements the problem is certainly very much simplified. That surface-tension may have much to do with catalysis is also in accord with the views of J. J. Thomson. He thinks that this might explain especially the action of the surfaces of the containing vessels on chemical reactions, changing the physical condition of the molecules in contact with the walls.

The older conception, that intermediate compounds are formed between the catalyzer, and at least one of the reacting substances, is untenable as a general theory of catalysis, and has given the place to a physical explanation of these remarkable phenomena.

PART III.

The reduction of unsaturated fatty acids
by different processes.

Alexander de Hemptinne of Belgium was one of the first to devise a practical process for converting oleic acid into stearic acid.

The process is based on the fact that olein and like compounds can be hydrogenized when subjected to the influence of electric effluvia. In this manner a considerable quantity of stearic acid may be formed according to the reaction $C_{18} H_{34} O_2 = C_{18} H_{36} O_2$.

During the process there are also formed polymeris of stearic acid and analogous compounds having melting points more or less in the neighborhood of $69^{\circ}C$, whereas olein is liquid at ordinary temperature.

The conversion may be effected by the use of the electric current in hermetically closed apparatus containing hydrogen maintained at a constant pressure by a suitable device.

Experiment has shown that it is preferable to operate at a pressure that is lower than that of the atmosphere.

The electric effluvia are produced between a series of metal plates arranged parallel and rather

close together. A plate of glass or other insulator must always separate two consecutive metal plates to avoid short circuiting and to produce uniform affluvia. Alternate metal plates are connected together and with one of the poles of the source of electricity by a conductor. Similarly the remaining metal plates are connected together and with the other pole.

By a device for sprinkling the plates, or by any other suitable arrangement the surface of the plates is covered with a thin mobile layer of olein, which is thus subjected in the presence of hydrogen to the action of the electric effluvia between the plates. Under these conditions the olein absorbs the gas, so as to form stearin in considerable quantity as well as other analogous substances of higher melting point than that of olein.

In 1907 Philipp Schwoerer of Germany devised what he calls an improved device for carrying out the well known process for transforming oleic acid into stearic acid under the action of hydrogen and in the presence of a finely distributed nickel as

catalytic agent.

As described by Sabatier and Senderens in their treatise on the catalytic action of finely distributed nickel, the output of the product rises with the temperature. The latter, however, is limited in the treatment of oleic acid in the vapor state, since at a temperature of about 270°C the decomposition of the fatty acids commences and the generated heavy volatile products of decomposition destroy the activity of the contact material. Moreover the product thus obtained could not be used directly in the manufacture of candles.

It has been found that by carrying out the above described reaction in the evaporator itself, the stated temperature will not be exceeded and can readily be controlled by the evaporating medium thus doing away with the difficulty of keeping up the temperature in a separate reaction chamber as well as with the special heating and care otherwise necessary.

The process is carried out in a cylindrical reaction chamber provided with a helical pan, extending from the top perpendicularly, nearly to the bot-

tom and is supported upon a central post. The oleic acid heated to 250° - 270°C runs down the helical pan and is drawn off below. The reaction chamber is jacketed and heated by superheated steam. The catalytic agent is applied to the bottom side of the helical pan, thereby effecting a continuous reaction of the oleic acid vapor with the hydrogen, without wetting the catalytic agent with liquid oleic acid, which would produce tar formation on it and thus disturb perfect reaction.

Superheated steam and hydrogen are used in the reaction chamber. The vapors from this chamber are condensed and the entrained hydrogen is returned to the process.

Fred Bedford of England uses a process whereby he converts unsaturated fatty acids or their esters into saturated acids or their esters respectively, or the reduction of nitro bodies, such as for instance, nitro benzole and ketones, for example benzo-phenome. The main object of his process is to increase the yield of reduced substance and to insure a thorough bleaching of the latter.

The vessel in which reduction takes place is under a vacuum. The vessel is in the form of a tower filled with nickel coated pumice stone. The nickel is used as the catalytic substance, being deposited on its support by reduction from nitrate. The nickel nitrate is reduced to oxide at a temperature between 275° and 300° C in a current of hydrogen. The reduction of the oleic acid takes place at from 160° to 200° C. The oil is sprayed in by means of hydrogen. The pressure in the chamber is below atmospheric pressure. The vapors go out thru the top and are condensed and fall into a receiver.

E. C. Kayser of Great Britain makes a special kind of a catalyzer. There are various ways for producing metallic powders in a state of fine division. Nickel powder which for many purposes is recognized as the most potent catalyzer technically available is most conveniently produced by acting upon such nickel compounds as the chloride, oxide, hydrate or carbonate at an adequate temperature with a reducing gas like hydrogen. The catalytic energy of such a powder

however, carefully prepared is at best an uncertain quantity, frequently it is feeble and sometimes for no conclusive reason, it is altogether lacking. Furthermore powder thus produced is specifically heavy and not easily kept in suspension in a liquid medium like oil, when that is desired, nor can it, since it forms an almost impervious sediment, be readily separated and recovered from such a liquid medium by a contrivance like the filter press. The same objections apply to nickel powder prepared by other means. Altogether, the difficulties of preparing reliable catalyzers and nickel catalyzers in particular, are well recognized and have largely prevented such catalyzers from gaining industrial importance.

It has been discovered that by bringing suitable soluble or insoluble compounds of nickel, such as the nitrate, oxide, hydrate or carbonate, in an appropriate manner, into intimate combination with an inert absorptive and comparatively bulky mineral substance, such as kieselguhr, infusorial earth, drying and com-

minuting the product and reducing the powder thus produced, highly efficient and reliable catalyzers may at all times be produced.

The catalyzers have moreover a comparatively low specific gravity, so that they can at will be readily suspended in a liquid medium such as oil. They also possess the great technical advantage of forming an excellent filter bed, and may in consequence be rapidly and completely recovered from the oil or other liquid, wherein they may have been suspended during use, by means of the filter press.

To develop the highest catalytic efficiency, the kieselguhr should become evenly and completely permeated and plated with a fine film of metal. Above and below this point of complete and even metalization beneficial results may still be secured, but the full benefit of this process and economy derived therefrom will not be realized.

The principal physical and mechanical considerations affecting the practical working of this process, are

to bring about and maintain, until the desired transformation be achieved, extensive contact between a mixture of metal and oil and the hydrogen gas, and moreover to produce such friction and impingement, as will enable the gas to penetrate to the recipient metal in spite of the repellent coating of oil. These conditions are attained by propelling in form of films or spray a comparatively small, but ever changing part of the hot oil mixture within an atmosphere of hydrogen. While this general principle should be embodied in all apparatus employed for the present purpose, there is considerable latitude in constructive detail

The preferred form of apparatus consists essentially of a closed horizontal cylindrical vessel, adapted to receive the hydrogen gas and to contain a comparatively small column of the mixture of oil and catalytic metal, in which cylinder is rotatably mounted a paddle wheel, or a plurality of such wheels having blades of wire gauze or equivalent material.

Water gas or hydrogen may be used under a pressure of one or more atmospheres. The temperature is maintained between 150°C and 160°C and the chamber is steam jacketed.

Carl Paal of Germany was the first man to use a catalyzer such as a metal or its salt in the reduction of an unsaturated body.

He says in part that the reduction of fats and unsaturated fatty acids of animal and vegetable origin may be effected by allowing hydrogen to act on the fats or fatty acids in presence of platinum metals or protohydroxid compounds of same, which have been deposited upon certain finely divided substances and act as catalyzers or carriers of hydrogen. It has now been ascertained that the reduction of the fats and fatty acids may also be effected by hydrogen in presence of solid salts of the platinum metals. Both the simple salts, such as palladium protochloride (Pd Cl_2), Platinum protochlorid (Pt Cl_2), platinum chlorid (Pt Cl_4), platinum hydrochlorid ($\text{H}_2\text{Pt Cl}_6$), platinum sulphate; and the double salts for instance potassium chloroplatinate (K_2PtCl_6), copper platinochlorid, may be used.

When the double salts are used, care must be taken that no anticatalytic substances, such for instance as lead, find their way into the reduction chamber. Use may be made of salts whose acid radicals or other constituents are themselves reduced by hydrogen, for example acid platinous oxalate.

All that is necessary to insure the action of the solid salts of the platinum metals is that they must be present in the solid form during the progress of the reaction. The salts may also be added to the fats in a dissolved condition, for example in an aqueous solution, the solvent being evaporated before or at the beginning of the reduction process. A suspension of the solid salts may also be used. For example the salts of the platinum metals may be triturated with the fat or oil that is to be reduced. Again, for example, a suspension of the salts in hydrocarbons, or mineral oil products, may be prepared, and this mixture be added to the substances that are to be reduced, in which case the suspensory medium may be eliminated during the process of reduction. A single salt of a platinum metal may be

used, or several salts and even several platinum. metals may be mixed together: and the salts may also be used in conjunction with the platinum metals which have been deposited on carriers, devoid of anti-catalytic action, such as copper, nickel carbon or magnesium carbonate. It is probable that, during the process, the salts of the platinum metals are split up into metal and free acid.



In any case however the solid platinum metal salts greatly facilitate the absorption of hydrogen by fats and fatty acids. Very small quantities of the platinum metal salts are sufficient to reduce large quantities of fat or fatty acids in presence of hydrogen.

When the reduction process is completed the platinum metals or their compounds can be easily separated from the molten reduced fat or fatty acid by filtration, and used again, either directly or after conversion into the solid state, as catalytic agents for the reduction of fresh quantities of fat or fatty acid.

If it is desired to prevent the formation of free

acid, as for example, hydrochloric acid from the chlorides of the platinum metals, in the reducing process, all that is needed is to add to the powdered platinum metal salts a neutralizing agent, such as anhydrous soda, in sufficient quantity to combine with the liberated acid. The addition of salts of the platinum metals assists the reduction process considerably more than is done by palladium black or platinum black containing an amount of platinum metal equal to that in the platinum metal salts added in the present method. Thus, for example, 1.7 parts of Pd Cl_2 (= 1 part of Pd) in presence of hydrogen will convert 10,000 parts of fat or fatty acid into solid masses within 3 to 4 hours. If, however, the Pd Cl_2 be replaced by a quantity of palladium black containing the same amount of palladium, then with a ratio of one part of Pd to 10,000 parts of fat or fatty acid, these substances will remain liquid, even when the palladium and hydrogen are allowed to act for twice or three times as long as in the experiment with Pd Cl_2 . Under these experimental conditions no appreciable action takes place when an attempt is made to

replace the palladium salt by palladium black.

The time required for the reduction depends on the amount of the platinum metal salt used and on the pressure under which the hydrogen is allowed to act. By using a palladium salt as the hydrogen carrier, about 50,000 parts of fat or unsaturated fatty acid can be hydrogenized within from 6 to 8 hours with a quantity of salt, for example Pd Cl_2 , corresponding with one part of Pd.

Example: One million parts by weight of oleic acid are treated with thirty-four parts by weight of dry palladium protochlorid (= 20 parts of Pd) in the form of powder with or without the equivalent amount of anhydrous soda; or with a 140 parts by weight of dry platinum protochlorid, all with or without addition of equivalent amount of anhydrous soda. The mixture is placed in a pressure vessel, from which the air is exhausted as completely as possible, and hydrogen is then admitted into the vessel under a pressure of 2 to 3 atmospheres. The reduction mixture is preferably kept in motion, which can be effected by means of a

stirring apparatus arranged in the pressure vessel. The vessel is heated to 80°C , although the reduction may be carried out at a lower temperature. The progress of the reduction, that is to say the consumption of hydrogen, is revealed by the fall in pressure as indicated by the pressure gauge. When the gauge registers only a low pressure a fresh quantity of hydrogen is admitted. The completion of the reduction process can be recognized by the gas pressure remaining constant for some considerable time.

Mose Wilbuschewitsch of Russia, uses for the reductive oleic acid, a series of chambers, steam jacketed and maintaining a temperature between 100° and 160°C . The oil catalyzer and hydrogen are sprayed in under a pressure of 9 atmospheres. The pressure is gradually lowered in the following chambers. The degree of reduction he gets depends on the chamber from which he draws the fat. The last chamber contains completely reduced fat.

The hydrogen from the last chamber is returned to the process.

The catalyzer is recovered by centrifugal action,

regenerated and returned to the process. This catalyzer is evidently a colloidal suspension.

Carleton Ellis of United States has a process whereby he uses practically the same catalyzer as others but has a counter stream of oil and catalyzer against a stream of hydrogen in a long and narrow tube.

Fred Bedford of England has a new process whereby he uses nickel oxid in suspension. The hydrogen is forced in thru the perforated bottom and up thru the oil. The chamber is heated by a closed steam coil 0.5 Kgs. of fine nickel oxid reduce 50 liters of oil in $5\frac{1}{2}$ hours. The oxid is not reduced in this process. He also uses cobalt oxid.

A. A. Shukoff of Russia passes nickel carbonyl into the oil to be subjected to the action of hydrogen at a temperature above the decomposition point of nickel carbonyl.

PART IV.

Fundamentals of preceeding theory and practice to
to be considered in carrying on experimental work.

FUNDAMENTALS.

After reviewing the various theories and work of men in the field of pure and applied science, one forms an opinion as to how one would attack the problem of "The Reduction of Cottonseed Oil," based on the theories of chemistry, mechanics, electricity and design involved.

An organic body having one or more carbon atoms with a double bond and known as an unsaturated body is under certain conditions easily reduced to a saturated compound.

The conditions most favorable for addition of H to the C are not fully understood. The constituent of this reduction which is the hardest to control and about which there is the least known is the catalyzer.

There are certain elements which seem to have greater catalyzing powers than others. Its chemical and physical state are also large factors in the action. The element in a finely divided state is the most efficient. By finely divided, we mean, so divided that when in a water solution and placed under a microscope the finely divided or colloidal suspen-

sion appears as a homogenous liquid. The most efficient metal is palladium followed closely by platinum and nickel. So little work has been done to date on the subject of the catalytic action of metals that in a few years we may find metals far more efficient than the above.

Another method of suspending the catalyzer is by means of Kieselguhr or infusorial earth. This is done by treating the Kieselguhr with a solution of the salt, drying and comminuting the product.

The object in preparing the catalyzer is to present as large a surface as possible to the oil. Therefore the more finely divided the larger the surface presented by a given amount of the metal.

The oil itself, or the vapor may be brought into contact with the catalyzer. The oil decomposes at 270°C . The temperatures at which the reduction is carried on varies from 100° to 300°C . The most successful commercial process keeps the temperature at 150°C to 160°C . The refined oil is the most desirable to use as it does not form a

tarry coating on the catalyzer as soon as the crude oil. This tarry coating makes the catalyzer sick and then it has to be regenerated. It is very desirable to bring the oil into the reduction chamber in as finely divided condition as possible. This is accomplished by numerous screen paddles or atomizer.

The hydrogen is used under a pressure of from 9 atmospheres to less than one atmosphere. The hydrogen may be introduced in the form of water gas, or mixed with steam, or mixed with air. In almost all cases the hydrogen leaving the reduction chamber is returned to the process. The hydrogen must escape to some extent for these are undesirable gases formed during the reduction which must be allowed to escape and therefore they must carry some hydrogen with them.

While these processes are many and varied in details they are all striving towards the most intimate contact of cottonseed oil, hydrogen and catalyzer at the best temperature for the most efficient result.

PART V.

Method of procedure in the reduction of
cottonseed oil.



PLATE I.

Method of Procedure.

Introduction.

After an exhaustive investigation of the literature and securing of all available data concerning the reduction of cottonseed oil a plan for carrying out this reduction was drawn up. Then after looking over the available apparatus and material at hand another plan of action was drawn up. Several of these plans were written as the details were studied and we thought we could improve the process. During operations the plans and methods were frequently changed.

Apparatus for Reduction and Filtering.

A photograph of this apparatus is shown on page Plate I. The machine was built with simplicity as the main object. Too complicated a machine would require too much time in construction.

The reduction chamber was made very long in proportion to the diameter. As the hydrogen enters the bottom thru a 1/4" pipe and passes up thru the oil it keeps the catalyzer and oil well stirred. The hydrogen is in contact with the oil for a long time,

due to the ratio of length of chamber to diameter of chamber. There is a thermometer tube, pressure gauge and 1/4" pipe connected to this chamber at the top.

All gases are absorbed to some extent by all liquids, the amount of gas absorbed varying greatly with the nature of the gas and also with that of the liquid. A given gas is absorbed by a given liquid to a very different extent under different conditions. It is well known that the greater the pressure to which the gas is subjected, the larger the amount dissolved. According to Henry's law, the amount of gas dissolved by a liquid is proportional to the pressure to which the gas is subjected. This law has been tested at pressures ranging from one to four atmospheres and was found to hold quite closely.

The pressure gauge thus gives the pressure under which the hydrogen is working, and by means of the thermometer cup the temperature of the oil may be determined.

It was thought at first that illuminating gas

which contains 30% H could be used. This idea was abandoned because of the low pressure in the gas mains and no means of pumping it into the reduction chamber under pressure.

Pure hydrogen gas in cylinders containing 320 cubic feet under 150 atmospheres was used. The hydrogen passed from the cylinder, thru meter, safety flask, valve and into bottom of reduction chamber. From the top of the reduction chamber the gas passes out thru a 1/4" pipe, thru safety chamber and gate valve to the atmosphere.

By means of valves live steam or air could be turned into the reduction chamber thru this 1/4" pipe.

The reduction chamber was steam jacketed and reequipped with gauge.

The filter press was the same as the reduction chamber, except that it was shorter and had a flange union at the bottom for a perforated plate and canvas.

By air pressure the oil from the reduction cham-

ber was sent to the filter press thru a pipe in the bottom of the reduction chamber to top of filter press.

The filter press could be worked automatically and independently of the reduction chamber.

This filter press worked too slowly, due to the earth clogging the canvass. It took four hours and 15 minutes to filter press 1000 c c of product.

The best press for this purpose is a hydraulic press, using bags.

Preparation of Catalyzers.

Colloidal Suspension of Platinum in Water.

To prepare a colloidal suspension of platinum in water, two platinum wires, one millimeter in diameter and weighing 1.2834 grains were used. A small crystalizing dish 3.2 cms. deep and 6 cms. in diameter was used. Each platinum wire was 1.5 inches long and connected to the electric mains by the ordinary set screw splices. A voltmeter was connected to read the drop across the platinum wire. An ammeter was connected in series. A single pole, single

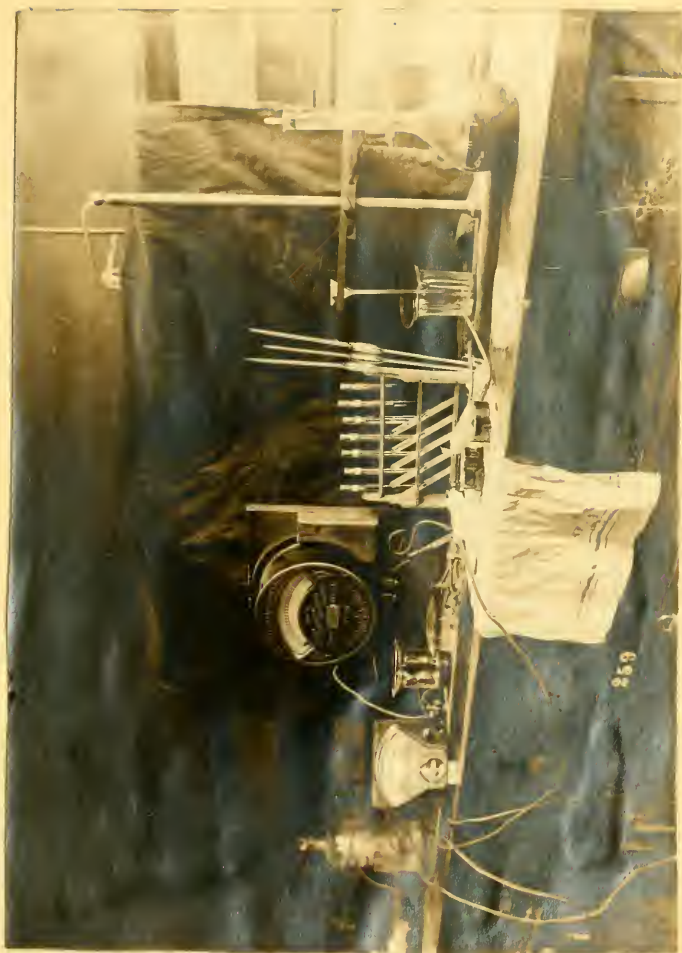


PLATE II.

throw knife switch was cut in the circuit close at hand for opening circuit when the platinum wires fused together. After much experimenting I was able to maintain a fairly constant arc by a rapid movement of the hands so as to cause a quick make and break. The amperes remained constant as well as the voltage.

Amperes	Volts
2.4	58

The drop before action over the line was 115 volts,.

Holding the two platinum wires in my hands with all other points on the circuit closed and using D.C.I. immersed the two platinum points $1\frac{1}{2}$ " below surface of the water. This closed the circuit, and then was quickly broken. An arc was thereby formed. At first the arc was obtained with great difficulty. Dark clouds rolled away and gave a dark brown color to the water.

The temperatures of the tips of the platinum wires determine the quality of the arc. When the points became red there was little of the platinum

going into solution and the wires tended to fuse together. Again the more rapidly and violent the contact, and the shorter the arc the more efficient the process.

No oxide formed on the platinum wires. A heavy black deposit occurred on the anode wire. This is platinum black. Also a globule was formed on the cathode. A slight deposit of platinum black occurred on the anode which as the action went on became pointed thus showing that the metal was being torn off the cathode and part going into solution and part depositing on anode as platinum and platinum black.

The temperature of the water rose rapidly. This caused a fairly rapid evaporation of the water. There was a loss of solution, due to splattering, which was not appreciable.

Reading of ammeter and voltmeter taken at maximum deflection.

E	I
80	0.6
10	1.2
35	0.6
35	1.0
30	1.6
10	0.6
5	0.8
15	2.0
5	0.8
5	0.6
5	2.8
5	3.4
5	3.6
30	2.6
40	0.6
20	2.8
25	2.8
5	2.4
15	0.6
5	3.4
5	2.0
5	1.6
3	2.6
2	2.4
5	2.6
1	2.6

These ammeter and voltmeter readings were not taken at the same time.

The arc was silvery white and illuminated the solution so that the fine particles of platinum sparkled with a silvery white luster, so that the solution had the appearance of the heavens at night with a myriad of stars twinkling. As the particles

were scintillating thru the solution they formed an interesting sight. The arc formed is from 0.5 m.m. to 1.5 m.m.

This water solution was filtered thru barium sulphate papers to remove the coarser particles which were torn off by the arc. The difference in weight of the platinum wires before and after arcing minus the weight of the ignited filter paper give the amount in the form of a colloidal suspension. One gram of this colloidal platinum reduces 10000 grams of oleic acid.

Colloidal Suspension of Platinum in Cottonseed Oil.

In this case we used refined cottonseed oil. The arc in this case appeared to be yellow and was blinding. Rapid action was impossible due to the blinding action of the arc. Dense black deposits were formed on the electrodes. This was due partly to platinum black and partly to decomposed hydrocarbons caused by the heating effect of the arc. It was necessary to shift the arc to avoid raising

the temperature to the flash point and causing dropping of the oil. This made it dangerous for the worker because hot oil feels uncomfortable on the skin and in the eyes.

Dark black fumes which are heavier than air rose and fell over the sides of the dish. A quick contact produced a cloud of platinum particles which rose to the surface in the form of a black ring. It was necessary to stir the oil to get the platinum mixed. The particles did not travel as fast in oil as in water, due to the viscosity of the oil. The colloidal suspensions in water and oil when placed under the microscope appeared to be homogenous.

Colloidal Suspension of Nickel in Oil and in Water.

In this case nickel wires were used for electrodes. When an arc was formed black clouds rolled away which on further investigation proved to be Ni_2O_3 . Evidently where a metal oxidizes easily it will form the oxide instead of a colloidal suspension.

Preparation of Catalyzer using
Kieselguhr.

In two runs the catalyzer consisted of two parts nickel and four parts clay, made as follows: Nickel nitrate was comminuted with the clay and roasted until the nitric acid was driven off. The product was again comminuted and put thru a 100 mesh screen. Enough clay was added to the oil to have 6% nickel oxide present. There was organic matter in the clay which in these cases was not entirely burned out. The proportion between Kieselguhr and nickel varied, as there are on the market many varieties of kieselguhr of diverse specific gravity and absorption power.

The next catalyzer was made as follows: Nickel nitrate solution was mixed with kieselguhr so as to have one part nickel to 4 parts clay. This was made into a thin mud by the addition of water, and then dried. After drying it was ground in a mortar to pass a 100 mesh screen. The product was then roasted to drive off all nitric acid and organic matter. It was again comminuted and was very easily

kept in suspension in water and oil. In this catalyzer the nickel was in a finely divided state and offered great surface for a given weight. It has been ascertained that nickel firmly and evenly deposited upon a voluminous, pulverous inert material exercises in a fluid medium a far more energetic action and much longer retains its vitality than an equal weight of pure metal in the finest state of division procurable.

Run No. I.

Compressed air was blown thru the machine to clean out all particles of dirt. Live steam was next blown thru to clean out all cement used in making the various joints tight. Live steam was then turned into the steam jackets. 800 c.c. of cottonseed oil was poured into the reduction chamber and all valves except the vent were closed. The temperature was brought up to 130°C. This was continued for 2 1/2 hours, and then run off by means of a valve in the bottom. This coated the inside of the machine with oil, and also helped to remove im-

purities.

Then measuring out 950 c.c. of Armour's refined cottonseed oil and adding catalyzer containing two parts nickel oxide to four parts clay, and so as to have 1% of nickel oxide by weight in the oil. It was thoroughly mixed. The catalyzer showed no tendency to settle out. This mixture was poured into the top of the reduction chamber. The vent valve was left open and the temperature brought up to 130° C at 50 pounds steam pressure. The hydrogen was turned on and passed thru the meter into the bottom of the reduction chamber, up thru the reduction mixture, thence thru the safety chamber and thru the vent valve to the atmosphere. Water vapor could be seen coming from vent pipe and there was an odor characteristic of hot cottonseed oil. A reading of the meter was taken. 33.45 cubic feet of hydrogen were used in this run which lasted three hours and fifteen minutes. Samples of the oil were taken every half hour.

After some time it was discovered that the oil

was disappearing. The temperature was not high enough to vaporize much of it and the question was, "Where had the oil gone?" The meter had run continually but not fast enough so that the oil had gone into the meter. This was the end of this run. A safety flask was placed between the meter and reduction chamber to prevent further trouble of this kind.

Run No. 2.

In this run 1000 c.c. of refined cottonseed oil were used. Enough of the catalyzer was used to form 1% of nickel oxide by weight of the cottonseed oil. The duration of this run was 6 hours and 82.1 cubic feet of hydrogen were used.

Time	Temperature °C	Pounds Steam
2:00	130°	40
2:30	135°	60
3:00	128°	45
3:30	131°	55
4:00	128°	50
4:30	132°	65
1:00	127°	45
1:30	128°	50
2:00	130°	50
2:30	132°	55
3:00	138°	70
3:30	128°	45

Samples were taken every hour. At the end of three hours the sample taken at that time was

cooled in tap water. Small white crystals separated out and the oil was cloudy. After some time it was thought that these particles might be stearin crystals. As it requires much time and a low temperature to chill the stearin out this was not attempted. A tube of original oil and three tubes of product were frozen for fifteen minutes by C O₂ gas. After the oil was warmed small white crystals were found on the sides of the test tube containing the product only. Also the product was cloudy which was due to a slight separation of stearin crystals.

These crystals could be placed under a microscope and the structure noted which would determine its identity.

The most accurate method is to take the iodine number of the original oil and of the product and thus it would give a quantitative result as to the quantity of oil reduced. This was done as shown in Results. The calculated iodine value of refined cottonseed oil is 111, but actual experiment shows

it to be 150. It is not just fully understood why the discrepancy. It might be due to formation of iodine addition products along the carbon chain.

Run No.3.

In this run 4 parts of clay and one part nickel oxide were used as described under catalyzers.

1000 c.c. of oil was used. This catalyzer seemed to be all that could be desired. The earth was evenly coated and had been heated to redness, comminuted and passed thru a 100 mesh screen. It remained in suspension for one hour without attempting to settle.

This reduction mixture was poured into the reduction chamber at 1:00 o'clock.

Time	Temperature	Pounds Steam
1:00	125°C	50
1:30	128°C	45

At 1:45 the supply of hydrogen gave out after having given up 132.25 cubic feet against the 320 which it was supposed to deliver. The machine was shut down until more hydrogen could be obtained.

Part VI.
Conclusions.

Conclusions.

The amount of stearin in the products of the different runs varied within wide limits. The product of the third run showed the greatest percentage of stearin.

The principle actors which determined the amount of stearin produced were, time of hydrogenization, pressure of the hydrogen, size of the particles of oil and catalyzer temperature, and the intimacy of contact of the oil, hydrogen and catalyzer.

There must be no elements present which would cause the catalyzer to lose its power.

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